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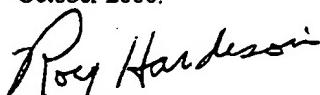
**TO: Betsy Hoey**  
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**PAGES: 12**

**DATE: 11/16/00**

Dear Ms. Hoey,

Here is a copy of a paper describing the use of CAPTOR® calcium thiosulfate solution for ozone quenching at the Burnt Cedar water treatment plant at Incline Village, NV, showing the date they started using the product. The paper was presented at the International Ozone Association, Pan American Group Conference at Orlando Florida in October 2000.



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# Improved Ozon Quenching With Calcium Thiosulfate

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## Abstract

The Burnt Cedar Water Disinfection Plant at Incline Village, Nevada uses ozone disinfection to meet the Surface Water Treatment Rule requirement for 3-log removal-inactivation of *Giardia* cysts and 4-log removal-inactivation of enteric viruses. The ozone disinfection system includes an oxygen storage and delivery system, ozone generators, a buried pipeline ozone contactor and an ozone quench system. The ozone quench system reduces dissolved ozone that remains in solution after primary disinfection is completed prior to adding chlorine as a final disinfectant. This paper presents operational experience with four ozone-quenching agents during the five year period between August 1995 and July 2000.

## Introduction

The Burnt Cedar Water Disinfection Plant (BCWDP) began disinfecting surface water from Lake Tahoe in August 1995. The BCWDP site is visible from the lake and is subject to strict aesthetic requirements. Most of the disinfection facilities were constructed at or below grade in order to meet water treatment requirements in the Surface Water Treatment Rule (SWTR) and stringent aesthetic requirements. The 8.5-million gallon per day (MGD) capacity BCWDP facility includes two liquid oxygen (LOX) storage tanks, two ozone generators, a raw water pump station, an ozone reduction system, an ozone contactor pipeline, an ozone quenching system, two treated water pump stations, a stand-by engine-generator and three chemical systems. The chemical storage and metering systems include an ozone-quenching agent system, a corrosion inhibitor system and a hypochlorite system. Additional information on the BCWDP is included in papers by Ryder (1993) and Thompson (1995 and 1996).

treatment system

The oxygen source for the ozone generators is stored in two 3,000-gallon LOX tanks. The LOX is converted to gaseous oxygen (GOX) in vaporizers mounted on the LOX tanks. The GOX flows to the operational ozone generator where oxygen is converted in a high-voltage electron stream to ozone. The ozone generators can produce an

zone-rich oxygen gas mixture then flows under a partial vacuum to the ozone transfer system. The ozone transfer system includes two booster pumps and four eductors. Three eductors provide the ability to add up to 100 pounds per day of ozone to the raw water at a six percent ozone gas concentration. The fourth eductor can recycle off gas if the zone concentration in the off gas is high (above one percent).

The ozone contactor is designed to provide at least 3-log inactivation of *Giardia* cysts and 4-log inactivation of enteric viruses with an average dissolved ozone concentration as low as 0.3 mg/L. The most challenging water treatment (disinfection) conditions occur when the source water temperature is at or below 5°C. The CT for 3-log *Giardia* inactivation at 5°C is 1.9 mg/L-minutes and the ozone half-life ranges between 7 and 20 minutes. Based on the available disinfection contact time and the maximum likely CT requirement, the ozone concentration in the water exiting the ozone contactor can be as high as 0.4 mg/L. The BCWDP design includes capability to add a reducing agent to the disinfected water to quench the residual ozone in the disinfected water after achieving the disinfection CT objective. The ozone-quenching agent is added to the ozonated water prior to adding hypochlorite, the final (secondary) disinfectant, and sodium silicate, the corrosion inhibitor, to the disinfected water and delivering it to the public via two treated water pump stations. There is between 24 seconds (at the maximum plant flow rate) and over two minutes (at the minimum plant flow rate) of reaction time for the quenching agent to reduce the dissolved ozone concentration between the point where the ozone-quenching agent is added to the disinfected water and the location where hypochlorite solution is added as the final disinfectant.

Treated water is delivered to the distribution system by between one and three of five treated water pumps. The treated water flow rate ranges between 1,100 and 6,000 gallons per minute (gpm) (between 1.5 and 8.5 MGD). The variable speed source water pumps' flow rate is paced to match the treated water pumps' combined flow rate. The disinfection contact time ( $T_{10}$ ) is inversely proportional to the flow rate through the ozone contactor pipeline. The dissolved ozone concentration in the disinfected water as it leaves the pipeline contactor disinfection section is a function of ozone dose, ozone demand, water temperature, hydraulic residence time and the ozone half-life. The ozone-quenching agent dose is adjusted to reduce the residual ozone concentration prior to adding chlorine to the disinfected water. One of the critical plant operating control goals is to add just enough quenching agent to reduce the dissolved ozone concentration but to also not add so much quenching agent that the residual (unoxidized) reducing chemical would react with chlorine added as a final disinfectant and reduce the chlorine concentration below an acceptable level.

The BCWDP is operated primarily as an unattended facility. A plant control PLC and SCADA system monitor the treated water and source water flow rates, dissolved ozone concentration and disinfection CT compliance. The plant control PLC adjusts the ozone generation rate to achieve disinfection requirements in a cost-effective manner and also controls the ozone-quenching agent metering rate based on a control signal from a dedicated dissolved ozone concentration analyzer (OCS-6).

## Background

The Incline Village General Improvement District (IVGID) Utilities Department began adding chlorine to disinfect the source water from Lake Tahoe and adding sodium silicate as a corrosion inhibitor prior to delivering treated water to the residential and recreational community along the northeast side of the lake in the early 1960's. This surface water supply is an extremely high-quality source water. The source water turbidity is typically below 0.2 NTU and ~~c~~liforms are seldom found. Watershed controls around Lake Tahoe (and the lake) serve as the first barrier to microbial contaminants. All wastewater generated in the Lake Tahoe basin is collected, treated and discharged outside the basin. This practice prevents nutrient accumulation and microbial contamination in the lake in order to protect the water quality in this beautiful oligotrophic lake. However, source water taken from Lake Tahoe for potable use must be treated to comply with microbial removal-inactivation requirements in the SWTR. The minimum treatment criteria for high-quality surface water sources such as Lake Tahoe is 3-log removal-inactivation of *Giardia* cysts and 4-log removal-inactivation of enteric viruses. New regulations in the United States Environmental Protection Agency (USEPA) Interim Enhanced Surface Water Treatment Rule (IESWTR) include *Cryptosporidium* removal criteria and add *Cryptosporidium* to the list of microbial contaminants that must be monitored in unfiltered water supplies. The Lake Tahoe watershed protection program includes monitoring for *Cryptosporidium* and adopting measures to control this difficult-to-disinfect microbial contaminant.

The USEPA and Nevada Division of Health approved filtration exemption with source water protection and disinfection as a means of meeting the SWTR requirements for Lake Tahoe water supplies in 1992. Domestic water supply systems with a filtration exemption must have deep water intakes located offshore away from streams discharging into the lake and must also complete a sanitary survey that includes multi-season source water quality monitoring that show potential contamination sources are and will be avoided. The IVGID water supply meets these criteria. The District elected to use ozone disinfection to meet the SWTR requirements as it provides a safe and palatable water supply at significantly less cost than a filtration process. The 8.5-MGD BCWDP was built on a 0.4-acre site adjacent to Lake Tahoe for less than \$3.5 million. One goal of the BCWDP design is that the treatment process should not change the mineral quality and would enhance the palatability of the water.

The SWTR combined 3-log *Giardia* and 4-log enteric virus removal-inactivation criteria are typically achieved through a combination of multiple physical barriers (clarification and/or filtration) and disinfection at most water treatment plants. The BCWDP meets the SWTR multi-barrier treatment objective with a combination of 1) watershed protection and a deep intake isolated from surface runoff discharges, and 2) ozone disinfection. Although the SWTR combined 3-log *Giardia* and 4-log virus removal-inactivation requirement is achieved entirely through ozone disinfection, chlorine is also added to the treated water to maintain a secondary disinfectant in the distribution system.

## **Water Treatment Facility**

### **Oxygen Source -Ozonation Generation System**

Two 3,000-gallon LOX storage tanks and two 33-standard cubic feet per minute (SCFM) capacity LOX-GOX vaporizers provide a reliable oxygen supply. The two LOX tanks provide capacity to permit receiving a full truck load delivery of LOX and to also maintain a reliable oxygen supply if one tank is taken off line for maintenance. The two 100 pound per day capacity ozone generators provide reliable ozone generation capacity. Based on plant operating experience, the ozone generators may also provide adequate capacity to meet a *Cryptosporidium* oocyst inactivation requirement, which may be included in either the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) or a Long Term 3 Enhanced Surface Water Treatment Rule. The ozone generator room includes space to install additional ozone generators if needed for additional disinfection capacity in the future.

### **Ozone Transfer System and Disinfection Contactor Pipeline**

A pipeline is the optimal contactor design for maximizing  $T_{10}$ , and hence disinfection CT credit. The  $T_{10}$  to hydraulic detention time ratio is defined by the USEPA to be 1 to 1 for a pipeline. The most effective method of transferring ozone into solution in a pipeline is with an eduction system. The BCWDP eduction system has capacity to transfer 100 pounds per day of ozone. Booster pumps normally provide the eductor motive water and the existing treated water distribution system provides a back-up supply of eductor motive water.

The ozone contactor pipeline is a cement-lined and coated steel pipe buried in a hillside above the lake. The cement used to line the ozone contactor pipeline includes a microsilica admixture to minimize both the permeability of the cement lining and corrosion of the carbon steel pipe. The ozone contactor pipeline was designed so that additional pipeline sections could be added to increase the length of the ozone contactor and hence the disinfection contact time if required to comply with a *Cryptosporidium* inactivation requirement in the future. The BCWDP design also permits adding filters if the filtration exemption for source water from Lake Tahoe is rescinded at a future date.

### **Ozone Quenching System**

The BCWDP ozone disinfection system was based on pilot plant data that indicated a "net ozone demand" (transfer inefficiency combined with actual ozone demand) for source water from Lake Tahoe of approximately 0.25 mg/L and an ozone half-life between 7 and 17 minutes for ozone dosages between 0.5 and 1.0 mg/L. The BCWDP ozone disinfection system was designed to provide an ozone dose as high as 1.2 mg/L to permit CT compliance for the most adverse operating conditions (coldest source water and an ozone half-life as low as 7 minutes), plus a 20 percent safety factor. A dissolved ozone concentration in the disinfected water as high as 0.25 mg/L was anticipated to comply with a 3-log *Giardia* and 4-log virus inactivation objective.

The ozone-quenching system is designed to reduce the ozone concentration in the treated water from as high as 0.4 mg/L to less than 0.01 mg/L. The nearest potable water customers are located within about 100 feet of the BCWDP and the treated water could contain noticeable concentrations of ozone if the dissolved ozone is not quenched. The ozone-quenching system is supposed to reduce the dissolved ozone concentration to non-detectable levels in order to prevent taste and odor complaints from near-by water users and also to minimize the risk that dissolved ozone would reduce the treated water pumps operating life. In addition, the ozone-quenching agent should not adversely impact treated water quality or the public perception of treated water quality. Some ozone-quenching agents were determined to be unsuitable to reduce the dissolved ozone concentration to less than 0.05 mg/L when the water temperature is low.

The ozone-quenching agent is added to the disinfected water near the end of the ozone contactor pipeline. The ozone contactor pipeline includes a 4,900 cubic feet (139 meter<sup>3</sup>) disinfection section located between the first and the fifth dissolved ozone monitor sampling points (OCS-1 and OCS-5, respectively) and a 320 cubic feet (9 meter<sup>3</sup>) ozone-quenching reaction section located between the fifth and the sixth dissolved ozone monitor sampling points. Chlorine is added to the disinfected water immediately after the sixth dissolved ozone sample point.

### Ozone-Quenching Agents

Four quenching agents have been used to reduce the ozone concentration in the treated water during the five year period between August 1995 and July 2000. The four ozone-quenching agents include:

1. Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>),
2. Sodium Metabisulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>),
3. Sodium Bisulfite (NaHSO<sub>3</sub>) and
4. Calcium Thiosulfate (CaS<sub>2</sub>O<sub>3</sub>).

### Stoichiometric Molar and Weight Ratios

The stoichiometric oxidation-reduction reactions that occur in water near a neutral pH and the corresponding weight ratios for the four ozone-quenching agents used at the BCWDP are summarized below.

#### *Hydrogen Peroxide*



Stoichiometric Weight Ratio: 34 gm/mole : 48 gm/mole = 0.7 : 1

#### *Sodium Metabisulfite*



Stoichiometric Weight Ratio: 190 gm/mole : 96 gm/2 mole = 2.0 : 1

## **Sodium Bisulfite**

The District used sodium bisulfite (bisulfite) for nearly three years (between April 1996 and February 1999) to quench the ozone residual. The stoichiometric bisulfite dose to dissolved ozone concentration weight ratio is 2.2 to 1. Operating experience at the BCWDP indicates that the bisulfite dose required to reduce the residual ozone concentration to an acceptable level was about 35 percent higher than the stoichiometric dose. Bisulfite has a similar impact as metabisulfite with respect to dissolved solids added to the treated water. The ozone-quenching oxidation-reduction reaction adds one mole of sodium ions and one mole of sulfate ions for each mole of ozone reduced by both metabisulfite and bisulfite. However, given the relatively small amounts of ozone to quench the increase in dissolved solids is negligible (< 1 mg/L).

Bisulfite is delivered in 55-gallon drums as a 25 percent solution containing approximately 2.5 pounds of dry sodium bisulfite per gallon and has a pH of 5. The 25 percent bisulfite solution is transferred from the drum to the ozone-quenching agent storage tank and added to the disinfected water using the existing chemical metering pumps. Although 25 percent bisulfate is a relatively stable chemical solution, it can release sulfur dioxide gas and will crystallize at temperatures below 60° F. The sodium bisulfite used at the BCWDP was not listed as a National Sanitation Foundation (NSF) Standard 60-compliant chemical.

## **Calcium Thiosulfate**

The District began using calcium thiosulfate (thiosulfate) as the ozone-quenching agent in February 1999 and currently continues to use thiosulfate to quench the ozone residual. Thiosulfate is available as a 24 percent solution containing approximately 2.5 pounds of dry calcium thiosulfate per gallon and has a pH of 7. The calcium thiosulfate solution used at the BCWDP is delivered in 220 gallon tote bins and is transferred from the tote bin to the existing 300-gallon tank in the ozone-quenching agent chemical storage and metering pump room about once per month. Between 45 minutes and 1 hour is required to transfer the tote bin contents to the storage tank, approximately 1/4<sup>th</sup> and 1/2 of the time previously required to prepare batches of metabisulfite and transfer bisulfite solution, respectively, each month. Calcium thiosulfate solution does not release sulfur dioxide (SO<sub>2</sub>) gas at temperatures below its boiling point (240° F), will not crystallize at temperatures above -9° C and will not freeze at temperatures above -30° C. The calcium thiosulfate used at the BCWDP has been tested by NSF and is certified to be suitable for use as a potable water additive in accordance with NSF Standard 60.

Although thiosulfate is a reducing agent, it would not reduce the dissolved oxygen concentration if discharged into a receiving water. An additional advantage of using calcium thiosulfate as an ozone-quenching agent for soft water such as the source water from Lake Tahoe is that increasing the calcium concentration in the water will also increase the Langelier Index and may help reduce treated water corrosivity.

**Table I – Alternative Ozonine Reducing Agent Properties**

Ozone Quenching Chemical	Hydrogen Peroxide ( $H_2O_2$ )	Sodium Metabisulfite ( $Na_2S_2O_5$ )	Sodium Bisulfite ( $NaHSO_3$ )	Calcium Thiosulfate ( $CaS_2O_3$ )
Material Type	Oxidizer	Reducing Agent	Reducing Agent	Reducing Agent
Ozone Reduction Reaction Rate	Slow	Fast	Fast	Fast
Handling Issues	Oxidant – fumes and contact	Dry chemical, solution prep., fumes and contact	Reducing agent fumes and contact, and pH	Container size <sup>d</sup>
Material requirements	316 stainless, hypalon, viton and teflon	PVC, Corrosive to brass and copper	PVC, Corrosive to brass and copper	PVC or CPVC, Corrosive to brass and copper
pH	Neutral	± 5	± 5	6.5 – 7.5
off-gases	$O_2$	$SO_2$	$SO_2$	No
Metering pump can lose prime due to off-gas	Yes	Yes	Yes	No
Low temperature crystallization	No	Yes	Yes	No
Stoichiometric Molar Ratio	1.0 to 1	0.5 to 1	1.0 to 1	0.25 to 1
Stoichiometric Weight Ratio	0.71 to 1	2.0 to 1	2.2 to 1	0.8 to 1
Cost per Dry Unit Weight	\$1.50 / pound	\$0.48 / pound	\$0.53 / pound	\$0.95 / pound
Chemical Cost <sup>a</sup>	\$13.25 / MG <sup>b</sup>	\$4.80 / MG <sup>c</sup>	\$5.30 / MG	\$5.55 / MG
Operating Cost <sup>e</sup>	\$14.25 / MG <sup>b</sup>	\$6.80 / MG	\$6.30 / MG	\$6.05 / MG

Note: <sup>a</sup> Cost of chemical to quench a 0.4 mg/L residual ozone concentration per million gallons (MG) disinfected based on operational quenching weight ratio at BCWDP.

<sup>b</sup> Includes additional cost to increase hypochlorite dose required to maintain chlorine residual in distribution system.

<sup>c</sup> Cost does not include labor to prepare solution from dry chemical.

<sup>d</sup> Requires mechanical assistance to move.

<sup>e</sup> Includes labor.

## **Plant-Scale Testing**

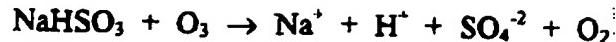
The performance of using hydrogen peroxide and sodium metabisulfite (metabisulfite) to quench ozone was evaluated in a plant-scale study conducted during January 1996. (Richey 1996) The ozone quenching study indicates that the peroxide to ozone weight ratio required to reduce the dissolved ozone concentration from about 0.2 mg/L to less than 0.1 mg/L is about 2.4 to 1. Based on operating experience at the BCWDP, the quenching weight ratio is 140 percent higher than the stoichiometric weight ratio. This study also indicates that unquenched ozone and the remaining peroxide react with chlorine added to the disinfected water as noted above. The chlorine dose had to be increased from the normal 0.5 mg/L to at least 0.8 mg/L in order to compensate for the ozone and peroxide oxidation-reduction reaction with chlorine. The ozone quenching study also indicates that the actual metabisulfite to ozone weight ratio required to reduce the ozone concentration from 0.2 mg/L to about 0.02 mg/L is 3 to 1. The plant-scale study indicates that the actual metabisulfite to ozone weight ratio required to reduce the dissolved ozone concentration to an acceptable level is about 50 percent higher than the stoichiometric weight ratio.

## **Sodium Metabisulfite**

The District used sodium metabisulfite (metabisulfite) for a two month period in February and March 1996 to reduce the ozone residual to less than 0.1 mg/L after completing disinfection. Switching from using hydrogen peroxide to metabisulfite, as the ozone-quenching agent, improved control of both the ozone disinfection system and the chlorine dosing system. Metabisulfite, and other sulfur-based reducing compounds, are oxidized by ozone to form ions that increase the dissolved solids in the treated water. Although, the stoichiometric weight ratio of metabisulfite to ozone is 0.5 to 1, the dissolved ozone concentration is generally so low that the amount of dissolved solids added to the treated water is relatively minor. The corresponding increase in dissolved solids is about 2.5 mg for each 1 mg of O<sub>3</sub> quenched. Operating experience at the BCWDP indicates that the metabisulfite dose required to reduce the residual ozone concentration to an acceptable level is about 50 percent higher than the stoichiometric dose. Therefore, the amount of solids added to the treated water (as sodium and sulfate ions) is less than 1 mg/L.

The metabisulfite used at the BCWDP is delivered as a dry chemical in 50-pound bags. Metabisulfite is added to the disinfected water from a 25 percent solution stored in a small batch tank. About 1 hour is required to prepare a batch of metabisulfite solution each week. The metabisulfite solution has a pH at about 5 and the plant operator must wear protective clothing while preparing each batch of metabisulfite solution. The operator safety equipment includes (as a minimum) goggles and a face respirator and the work area must have adequate ventilation. In addition, care must be taken while preparing a batch of metabisulfite solution to minimize the risk from chemical burns.

### **Sodium Bisulfite**



Stoichiometric Weight Ratio: 104 gm/mole : 48 gm/mole = 2.2 : 1

### **Calcium Thiosulfate**



Stoichiometric Weight Ratio: 152 gm/mole : 192 gm/4 mole = 0.8 : 1

Properties, requirements and operating costs of the four ozone-quenching agents used at the BCWDP are summarized in Table I.

### **Operating Experience**

The ozone disinfection system was designed to use hydrogen peroxide as both an ozone-quenching agent and to form hydroxyl radicals for control of the taste and odor compounds that are present in the lake water on rare occasions. However, when the residual ozone concentration in the disinfected water at the BCWDP exceeds 0.1 mg/L the ozone concentration in nearby portions of the distribution system exceeds 0.03 mg/L and is detectable in household tap water. Customer complaints have described the treated water as having a metallic chemical taste when some quenching agents were used.

### **Hydrogen Peroxide**

Hydrogen peroxide was used to quench the residual ozone during the pilot plant study and was selected as the initial ozone-quenching agent since it can quench ozone without increasing the dissolved solids in the treated water. Although hydrogen peroxide is sometimes an oxidant, it has a lower oxidation potential than ozone and will react with ozone as a reducing agent. Based on the pilot study data, hydrogen peroxide appeared to be a suitable ozone-quenching agent. (Thompson 1992) Hydrogen peroxide was also selected as the ozone-quenching agent since adding it to the disinfected water should not adversely impact the aesthetic quality of this excellent source water. In addition, hydrogen peroxide can react with dissolved ozone to form hydroxyl radicals ( $\text{OH}^-$ ), which could oxidize taste and odor causing compounds that can be present in the Lake Tahoe source water on occasions.

The ozone reduction reaction rate using hydrogen peroxide is slower than it is with sodium metabisulfite (metabisulfite), sodium bisulfite (bisulfite) and calcium thiosulfate (thiosulfate). The District has also used metabisulfite, bisulfite and thiosulfate, which are sulfur-based reducing compounds (electron donors), as the ozone-quenching agent. These three reducing compounds have faster oxidation-reduction reactions than peroxide does when used to quench ozone.

## **Summary And Conclusions**

Five years of operating experience at the BCWDP using peroxide, metabisulfite, bisulfite and thiosulfate as ozone-quenching agents provides insight regarding advantages and disadvantages of each of these four chemicals.

1. Hydrogen peroxide does not change the mineral characteristics of the source water, but has an ozone-quenching reaction rate that is too slow to meet operating goals when the water temperature is low.
2. Metabisulfite, bisulfite and thiosulfate have more rapid ozone quenching reactions than peroxide. Although all three of these sulfur-based ozone-quenching agents increase the dissolved solids concentration, the relatively small amount of dissolved ozone to be quenched and the actual weight ratio of quenching agent to ozone results in a relatively minor increase in dissolved solids in the treated water.
3. Sodium metabisulfite requires more labor to prepare than the three other ozone-quenching agents. It can release SO<sub>2</sub> gas and will crystallize at ambient temperatures.
4. Sodium bisulfite has a pH around 5, requires care in handling and can also release SO<sub>2</sub> gas.
5. Calcium thiosulfate is available as a NSF Standard 60-compliant product and does not release SO<sub>2</sub> gas or crystallize like the two other sulfur-based ozone-quenching agents.

Plant-scale evaluation of using hydrogen peroxide, sodium metabisulfite, sodium bisulfite and calcium thiosulfate to quench ozone indicates that calcium thiosulfate has significant advantages over the three other ozone-quenching agents for this low temperature and low alkalinity source water supply as summarized in Table I. Although the chemical cost of thiosulfate is slightly higher than the cost of the two other sulfur-based reducing agents per million gallons treated, plant staff indicate that the operational advantages of calcium thiosulfate more than off-set the slightly higher chemical cost of calcium thiosulfate. When the labor cost to prepare or transfer the ozone-quenching agent is included in an evaluation of operating costs, thiosulfate is a lower cost alternative than hydrogen peroxide or the two other sulfur-based reducing agents. Based on 5 years of operating experience, calcium thiosulfate appears to be the best ozone-quenching agent for the BCWDP.

## **Key Words**

Ozone; Disinfection; Ozone-Quenching; Sodium Metabisulfite; Sodium Bisulfite; Calcium Thiosulfate

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